

SOLUBILIZATION OF COALS BY NON-REDUCTIVE ALKYLATION IN LIQUID AMMONIA

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In a previous communication we reported that a major portion of a low rank vitrinite (80.8% C, daf) could be converted to chloroform soluble products by non-reductive ethylation in liquid ammonia (1). This paper presents the results of our more in-depth studies on non-reductive alkylation of five Cretaceous and two Carboniferous coals. To assist in understanding of the chemical aspects of the non-reductive alkylation, which has been only marginally explored in organic chemistry, a considerable amount of work was carried out on alkylation of various model compounds.

Experimental

The particle size of coal samples was reduced to below 300 mesh and, prior to reaction, the samples were dried in vacuo (13 Pascals) at 70°C. The reaction was conducted under protective cover of oxygen-free helium in 150 ml of vigorously stirred liquid ammonia containing sodium and potassium amides generated "in situ" by action of anhydrous ferric chloride (0.8-1.0 g) on metallic sodium (3.0 g) and potassium (3.0 g). Precautions were taken to ensure that a complete conversion of metals to the respective amides took place prior to addition of coal sample. The mixture was stirred for six hours. 100 ml of anhydrous ethyl ether was added and the contents were alkylated with 2.05 molar excess (on the combined alkali metals) of the desired alkyl bromide. Solvents and excess alkyl bromide evaporated overnight. The contents were acidified with 5 N hydrochloric acid, the product was washed thoroughly with cold water, extracted overnight with refluxing water and dried. Three successive ethylations were carried out on each sample of coal.

Alkylation of model compounds was carried out under similar conditions except that smaller quantities of ammonia (70-80 ml), ferric chloride (0.5 g), sodium (1.7 g) and potassium (1.7 g) were used. The amount of substrate was always the same (0.028 M). Reaction product was recovered either by filtration (solids), or by extraction with organic solvent (chloroform or ether). Products were analysed by GC, GC-MS and NMR spectroscopy.

Proton and C-13 spectra of soluble products (alkylated coals and model compounds) were recorded in CDCl_3 using Bruker WP-80 apparatus. For C-13 NMR spectra signal accumulation was necessary. C-13 spectra of solid coals were recorded in the Laboratories of the National Research Council, Ottawa, using a Bruker CXP-180 spectrometer and cross polarization-magic angle spinning technique.

Number average molecular weights of coal extracts and of their subfractions were determined in pyridine using Corona-Wescan vapour pressure osmometer and concentrations 1-20 g/Kg.

GPC fractionation was carried out on column of Sephadex LH-60, an hydroxypropylated dextran gel, 80 cm in length and 2.5 cm in diameter using chloroform as solvent.

Results and Discussion

Alkylation of Coals. The information regarding the origin and rank of coals tested and the results of alkylation studies conducted on these coals is summarized in Table 1. The number of alkyl groups introduced into coal varied from 7 to 18 per 100 original carbon atoms. The carboniferous coals tested in these studies appeared to be more susceptible to solubilization than their Cretaceous counterparts. Alkylation took place on both oxygen and carbon atoms. Depending on coal, the ratio of alkylated oxygen to alkylated carbon atoms varied from 0 (coal #5) to approximately 0.5 (coals #1, 2 and 3).

Long chain alkyl groups, n-butyl and n-hexyl, seem to alkylate hydroxyl groups more efficiently than short chain, ethyl groups. There is a residual level of hydroxyl groups which defies ethylation. No simple relationship exists between the number of alkyls introduced and the degree of solubilization.

Non-reductive alkylation of coal #7 led to high conversion of this coal to chloroform soluble product. Extraction of a small sample (0.5 g) of triply ethylated coal resulted in 63% solubility. However, when larger sample (10 g) was similarly extracted, the solubility was lowered to 48.1%. Essentially the same total solubility (49.6%) was obtained when ethylation was alternated with extraction after each of the three ethylation steps. Such experimental sequence will be referred to in this text as alternate ethylations 1, 2 and 3.

Number average molecular weights of fractions solubilized by either method are similar: 1260 for triply ethylated coal, and 1140, 1300 and 1250 for soluble parts of alternate ethylations 1, 2 and 3 respectively.

Gel permeation chromatography of solubilized fraction of triply ethylated coal showed that 8.7% of sample had molecular weight of 15,440; 11.2% - 10,430; 10.4% - 5,740; 12.3% - 2,570; 35.2% - 910 to 1,040; 10.4% - 875; 2.6% - 580; and 9% of sample was not recovered from the column, even after the polarity of chloroform was increased by addition of 1% ethanol.

NMR Spectra. NMR spectra of untreated solid coal #7 and of its solubilized fractions are reproduced in Figures 1-4. Comparison of

the aliphatic region of C-13 spectra of our fractions with C-13 spectra of solid coal, coal liquids and coal extracts published in literature (2, 3, 4) is made in Table 2. The most consistent and intense line is that at 29-30 ppm. Absorption bands at 9, 12 and 14 ppm are strong in the fractions of ethylated coal. These bands are associated with the methyl carbons of the introduced ethyl groups. This was proven conclusively by ethylation with D₅-ethyl bromide, which led to disappearance of these bands (Figure 3) together with elimination of much of the underlying hump in the 25-35 ppm region (methylene absorptions β to an aromatic ring; ref 5).

Noticeable difference between the C-13 spectra of non-reductive-ly solubilized coal and the spectra of fractions resulting from other methods of solubilization is the C-13 line at 46 ppm. Absorption band approximating this frequency is seen in the spectrum of solid coal of Zilm and co-workers (3). It is also present in coal #7. The environment responsible for this absorption was lost in other methods of solubilization but was preserved in our alternatively ethylated samples. The intensity of this spectral line increases progressively for solubilized fractions of alternate ethylations from 1 to 3. This strengthening of absorption at 46 ppm seems to be associated with a weakening signal at 29 ppm. Another relevant observation is that the line at 46 ppm is absent in triply ethylated coal. It also disappeared on second ethylation of soluble product from alternate ethylation 1. The above spectral observations could be interpreted in terms of changes in C-13 chemical shifts occurring on alkylation of structural unit of coal of a 9,10-dihydrophenanthrene (DHP) type.

Secondary carbons in 9 and 10 positions of 9,10-DHP absorb at 29 ppm. On ethylation, when both hydroaromatic carbons are transformed into tertiary carbon atoms (-CHR-CHR-) their C-13 absorption shifts to 46 ppm. Under conditions of exhaustive ethylation (triple ethylation of the same coal sample, and second ethylation of solubles of alternate ethylation 1) the easily accessible sites do not exist any more. The more difficult tertiary environments are then substituted which leads to disappearance of the spectral line at 46 ppm.

Ethylation of Model Compounds. Eight model compounds (adamantane, indan, dibenzyl, diphenylmethane, 9,10-dihydrophenanthrene, 9,10-dihydroanthracene, fluorene and acenaphthene) were ethylated under the conditions of non-reductive alkylation of coal. GC-MS and NMR analyses of the products provided information on relative reactivity of hydrogen atoms in these compounds (Table 3). Hydrogen atoms in polycyclic condensed network of adamantane are unreactive. Negligible monoethylation (0.1%) occurred in indan. Ethylation of dibenzyl was low, and that of 9,10-DHP only moderate. Activation of methylene group by two phenyl rings makes the hydrogen quite reactive in liquid ammonia. Activation by phenyl ring and an olefinic bond as in indene (an impurity in indan) is also effective. Hydrogen atoms in 9 and 10 positions of dihydroanthracene and in 9 position of fluorene substitute very readily.

Acenaphthene produced a puzzle: all of it reacted to give multiple isomers of di-, tri-, tetra-, and even penta-ethylated compounds. Ten major and at least twenty minor components resulted. Work on their identification is now in progress.

The C-13 spectra of ethylated coal and of some of the model compounds have absorption lines upfield to 8.4 ppm. These are the absorption lines of the methyl carbons δ to an aromatic ring. The presently known upfield absorption limit for the δ methyl groups extends only to about 10 ppm (6). In addition to 8.5 band in the ethylated coals, the high field absorption was observed for the methyl carbon in diethyldiphenylmethane (8.4 ppm), 9,9,10,10-tetraethyl-9,10-dihydroanthracene (8.6 ppm) and 9,9-diethylfluorene (8.5 ppm). C-13 absorption in the region of 46 ppm was observed for 9,10-diethyl-9,10-dihydrophenanthrene (46.3 ppm); 9,10-diethyl-9,10-dihydroanthracene (48.4 ppm) and in 1-ethyl-1,2-diphenylethane (carbon 1-49.9 ppm; carbon 2-43.6 ppm).

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Table 1. Summary of the Alkylation Data

Coal No.	Origin	ZC, daf	Alkyl group used	Solubility, wt% daf		OH groups/100 C atoms			Alkyl groups/100 C atoms after each alkylation calculated from:		Final no.* of alkyl groups on:							
				initial	after 3 alkylations	initial	after alkylation	1	3	ΔW	ZH	C	O					
CRETACEOUS COALS																		
1.	Saskatchewan	73.9	ethyl	2.9	24.5			6.6	4.3	2.8	7.0	9.1	11.8	7.4	-	14.8	9.5	3.8
2.	Alberta	77.7	ethyl	3.0	33.2			5.5	-	1.7	8.6	15.9	17.8	5.4	6.4	7.5	8.8	3.8
			n-propyl		33.0			5.5	2.1	1.4	7.7	11.4	13.1	8.0	11.7	14.3	9.6	4.1
			i-propyl		30.7			5.5	3.1	2.8	5.6	7.9	9.7	4.7	-	8.2	6.2	2.7
			n-butyl		38.5			5.5	3.2	1.2	9.0	11.5	12.7	6.3	9.5	12.2	8.1	4.3
3.	British Columbia	80.6	n-hexyl		35.7			5.5	-	0.3	11.7	13.6	15.0	9.0	14.0	16.9	10.7	5.2
			ethyl	3.6	25.9			4.8	-	1.4	6.3	8.7	10.5	4.4	6.2	7.3	5.5	3.4
4.	Alberta	86.8	ethyl	3.6	28.0			1.1	0.4	0.4	5.9	7.7	9.0	4.2	6.0	7.0	7.3	0.7
5.	British Columbia	88.8	ethyl	3.8	28.9			0.3	0.3	0.3	5.8	7.9	9.5	8.1	-	12.5	11.0	0
CARBONIFEROUS COALS																		
6.	West Virginia	83.2	ethyl	6.3	39.0			2.3	1.6	0.9	11.7	13.0	14.4	5.6	-	12.6	12.1	1.4
7.	Freeport seam	87.3	ethyl	3.2	63.6			1.1	0.7	0.5	5.1	7.5	8.4	4.1	-	7.3	7.2	0.6

*per 100C atoms, using the average of ΔW and ZH after three alkylations

Table 2. Aliphatic Region of C-13 NMR Spectra of Coals and Some Coal Derived Products

Sample	Chemical Shifts, ppm from TMS									
coal #7 (solid)	-46-43*				-30**			-19-	-14-11-	
coal (solid) (3)	-44-				-29-			-20-15-		
coal extract (2)	37.8	32.4	<u>30.2</u>	29.8	23.1	21.5	19.1	14.2		
(2)		31.9		<u>29.7</u>	22.7	21.4	19.8	14.1		
coal liquid (3)	33			<u>29</u>		22	20	17	15	
coal liquid (4)			31	30		22		15		
triply ethyl ^d #7	37	32		<u>29.5</u>	22.5	21.5		-14-12-9-		
triply D ₅ -ethyl ^d #7	43	37	32	<u>29.7</u>	23	21.5	19	14		
alt. ethylation 1	46	37	33	32	<u>29</u>	23	22	19	15	14 -9-
alt. ethylation 2	<u>46</u>		32	31	<u>29</u>		22		15	14 -8.5-
alt. ethylation 3	<u>46</u>				29	28	22		15	14 12-9-
alt. ethylation 1 ethylated again		-33-			<u>29</u>		-22-		-15-14-12-	<u>8.5</u>

*-43-indicates a broad band with a maximum, for example, at 43

**underline indicates a high intensity absorption

Table 3. Summary Information on Ethylation of Model Compounds

Model Compound	Molar Ratio*	% Conversion	Aliphatic C-13 nmr shifts of _____				
			originally present C modified by ethylation	introduced ethyl			
			C	CH	CH ₂	CH ₂	CH ₃
Adamantane	1.07	NR**					
Indan	1.07	99.9 NR 0.1 mono-					
Dibenzyl	1.07	98 NR 2 mono-		49.9	43.6	28.4	12.0
Diphenyl-methane	2.14	93.6 mono- 6.4 di-		53.4	-	28.6 29.4	12.8 8.4
9,10-Di-hydrophenanthrene	1.07	66.7 NR 24.7 mono- 8.6 di-	- -	40.2 46.3	33.6 -	26.2 27.9	12.0 12.2
9,10-Di-hydroanthracene	1.07	53.4 di- 24.3 tri- 22.3 tetra-	-	48.3	-	35.2	13.3 8.6
Fluorene	2.14	100 di-	56.2	-	-	32.8	8.5

* moles of combined alkali metals to moles of hydrogen on ~~on~~ carbon to an aromatic ring

** NR - no reaction

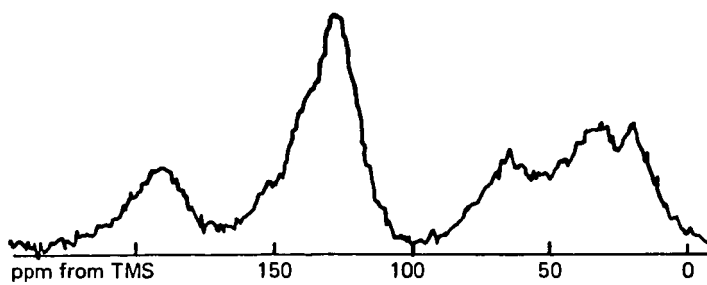


Figure 1. C-13 nmr spectrum of solid coal no. 7.

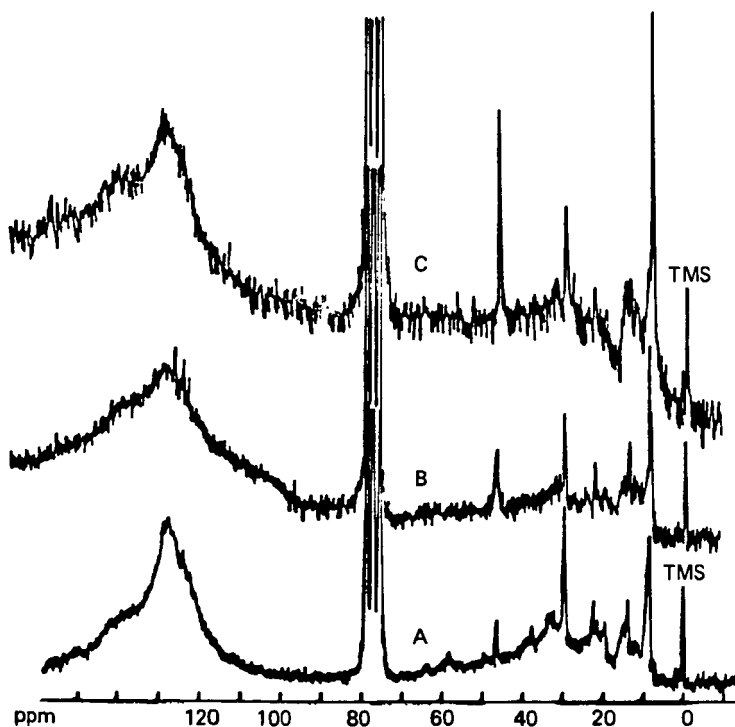


Figure 2. C-13 nmr spectra of solubilized coal no. 7 after:
A-first alternate ethylation; B-second alternate
ethylation; C-third alternate ethylation.

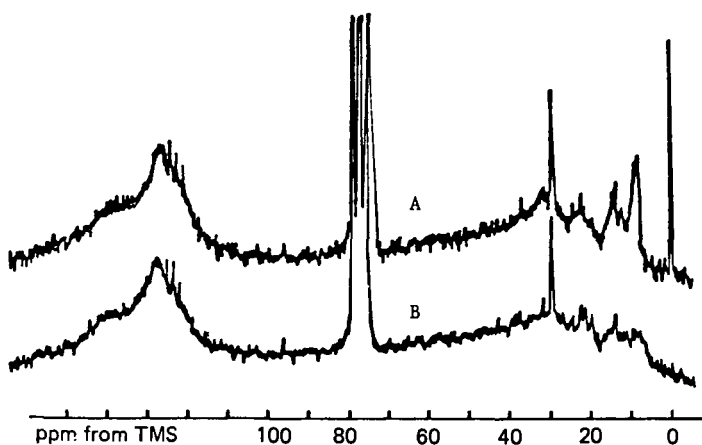


Figure 3. C-13 nmr spectra of solubilized coal no. 7 after:
A-triple ethylation; B-triple D₅-ethylation.

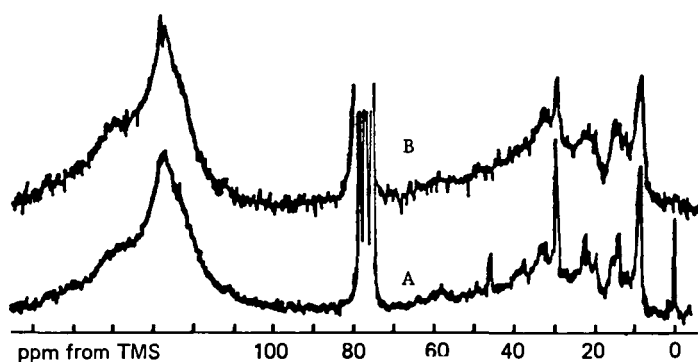


Figure 4. C-13 nmr spectra of solubilized coal no. 7 after:
A-first alternate ethylation; B-sample A ethylated
once more.